STUDIES ON ELECTROCHEMICALLY SYNTHESIZED POLYANILINE AND ITS COPOLYMERS

ALI PARSA

UNIVERSITI SAINS MALAYSIA
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STUDIES ON ELECTROCHEMICALLY SYNTHESIZED POLYANILINE AND ITS COPOLYMERS

by

ALI PARSA

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LIST OF ABBREVIATIONS

AA	Ascorbic acid
Ani	Aniline
B	Benzenoid
CG	Composite Graphite
CVs	Cyclic Voltammograms
DMF	*N,N* – Dimethylformamide
DPPH	1,1-diphenyl-2-picrylhydrazyl
E_{ap}	Applied Potential
EB	Emeraldine Base
EDX	Energy Dispersive X-ray
E_p	Peak Potential
E_{pa}	Anodic Peak Potential
EQCM	Electrochemical Quartz Crystal Microbalance
ES	Emeraldine Salt
ESCA	Electron Spectroscopy for Chemical Analysis
I_{pa}	Anodic Peak Current
LEB	Leucoemeraldine Base
LSV	Linear Sweep Voltammetry
MeOH	Methanol
*m*PDA	*meta*-Phenylenediamine
OFN	Oxygen-Free Nitrogen
*o*PDA	*ortho*-Phenylenediamine
PAni	Polyaniline

PDAs	Phenylenediamines
PE	Protonated Emeraldine
PNB	Pernigraniline Base
P*o*PDA	Poly-*ortho*-phenylenediamine
*p*PDA	*para*-Phenylenediamine
PPDAs	Polyphenylenediamines
PPy	Polypyrrole
PTSA	*para*-Toluene Sulphonic Acid
Py	Pyrrole
Q	Quinoid
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy

KAJIAN TERHADAP SINTESIS ELEKTROKIMIA POLIANILINA DAN KOPOLIMERNYA

ABSTRAK

Pengelektropolimeran oksidaan anilina di dalam asid fosforik di atas grafit komposit pensil 2B telah disempurnakan dengan menggunakan beberapa garam takorganik yang dipilih sebagai elektrolit penyokong. Garam-garam ini menentukan darjah kekonduksian polianilina yang terbentuk mengikut turutan $CaCl_2$ > KCl > $ZnCl_2$ > $ZnSO_4$ > $Ca_3(PO_4)_2$. Kehadiran samada 0.06 M $Ca_3(PO_4)_2$ atau 0.2 M $ZnSO_4$ di dalam sintesis polianilina telah menyebabkan anjakan puncak redoks sebanyak 250 mV ke keupayaan negative. Anjakan puncak ini hanya dipengaruhi oleh jenis-jenis anion yang ada bukan nya kation. Kejadian ini memudahkan pembentukan kopolimer Ani dan *orto*-fenilindiamina.

Morfologi lapisan nipis homopolimer polianilina juga telah diperiksa dengan mikroskop imbasan elektron pemancaran medan dan penyebaran tenaga pembelauan sinar-X. Keputusan menunjukkan morfologi permukaan homopolimer bergantung kepada elektrolit yang digunakan. Morfologi permukaan juga menentukan pembentukan hablur seperti bunga yang berbeza setiap garam takorganik.

Sintesis homopolimer di dalam garam yang berbeza menambah keupayaan antioksidan. Polianilina dalam medium fosfat adalah agen penurunan yang kuat, berupaya mengaut radikal 1,1-difenil-2-pikrilhidrazil dalam metanol. Ia nya dua kali lebih berkesan sebagai antioksidan daripada polianilina dalam medium klorida.

Penyediaan anod homo dan pengkopolimeran anilina dan pirola di atas grafit komposit di dalam asid para-toluena sulfurik akueus dengan dan tanpa kalium klorida (KCl) telah dilakukan. Kehadiran KCl di dalam medium telah meningkatkan

sifat struktur, optik dan morfologi polimer yang dihasilkan. Spektroskopi fotoelektron sinar-X membuktikan sintesis poli(anilina-*ko*-pirola) dengan kehadiran KCl mempunyai hampir setara unit pirol dan anilina di dalam tulang belakang polimer berbanding sintesisnya tanpa kehadiran KCl.

Anjakan negatif inheren puncak redoks polianilina telah juga dilakukan di dalam pengkopolimeran anilina dengan *orto*-fenilinadiamina di atas grafit komposit. Grafit komposit terubahasuai poli(anilina-*ko*-pirola) menunjukkan gerak balas pengelektromangkinan terbaik terhadap pengoksidaan asid askorbik. Keupayaan puncak anod asid askorbik telah beranjak dari +0.5 V vs. Ag/AgCl (pada grafit komposit) ke +0.1 V vs. Ag/AgCl (pada grafit komposit terubahsuai poli(anilina-*ko*-pirola)), menunjukkan proses elektod yang mudah bagi asid askorbik pada grafit komposit terubahsuai.

STUDIES ON ELECTROCHEMICALLY SYNTHESIZED POLYANILINE AND ITS COPOLYMERS

ABSTRACT

Oxidative electropolymerization of aniline in phosphoric acid on 2B pencil composite graphite was accomplished using some selected inorganic salts as supporting electrolytes. These salts determined the degree of conductivity of polyaniline formed, in the order of $CaCl_2$ > KCl > $ZnCl_2$ > $ZnSO_4$ > $Ca_3(PO_4)_2$. The presence of either 0.06 M $Ca_3(PO_4)_2$ or 0.2 M $ZnSO_4$ in the synthesis of polyaniline have caused the shifting of its redox peaks as much as 250 mV to the negative potential. The shifting of these peaks was only influenced by type of anions presence not the cations. This incident has prompted the formation of copolymer aniline and *ortho*-phenylenediamine.

The morphology of the homopolymer polyaniline films was also examined by a field emission scanning electron microscope and energy dispersive X-ray diffraction. The results showed that surface morphology of the homopolymer was dependent on the electrolytes used. The surface morphology also dictated each inorganic salt into different bloom-like crystal formations.

The homopolymer synthesised in different salts has its antioxidant capacity increased. The phosphate medium polyaniline was a strong reducing agent, capable of scavenging 1,1-diphenyl-2-picrylhydrazyl radical in methanol. It was twice more effective as an antioxidant than the chloride medium polyaniline.

The anodic homo and copolymerization of aniline and pyrrole on composite graphite in aqueous *para*-toluene sulphonic acid with and without potassium chloride (KCl) were investigated. The presence of KCl in the medium has improved the structural, optical and morphological properties of the resulting polymers. The X-ray

photoelectron spectroscopy confirmed that poly(aniline-*co*-pyrrole) synthesized in the presence of KCl has nearly equal units of both pyrrole and aniline in the polymeric backbone as compared to the one synthesized in absence of KCl.

The inherent negative shift of redox peaks of polyaniline has also been investigated in the copolymerization of aniline and *ortho*-phenylenediamine on composite graphite. The poly(aniline–*co*–*ortho*-phenylenediamine) modified composite graphite showed excellent electro catalytic response towards the oxidation of ascorbic acid. The anodic peak potential of ascorbic acid has been shifted from +0.5 V vs. Ag/AgCl (at bare composite graphite) to +0.1 V vs. Ag/AgCl (at poly(aniline–*co*–*ortho*-phenylenediamine) modified composite graphite), indicating easier electrode process of ascorbic acid on the later.

CHAPTER 1

INTRODUCTION

1.1. History of conducting polymers

Conducting polymers are relatively new class of materials whose interesting metallic properties were first reported in 1977, with the discovery of electrically conducting polyacetylene [1]. The importance of this discovery was recognized in 2000 when the Nobel Prize for Chemistry was awarded to the scientists who discovered electrically conducting polyacetylene in 1977 [2]. Since the discovery of polyacetylene, there has been much research into conducting polymers and many new conducting polymers have been synthesized. The most important, and common of these are polypyrrole [3], polyaniline [4], polythiophene [5] etc. There have been many potential applications suggested for these materials, including sensors [6, 7], electro-chromic devices [8, 9], corrosion inhibitor [10, 11], supercapacitor [12, 13], electromagnetic shielding [14, 15], polymeric batteries [16], polymeric actuators [17, 18], etc. These wide ranges of applications are possible in part due to the ability to alter the electrochemical, optical, chemical and mechanical properties of conducting polymer by changing the monomer and or dopant incorporated into the polymer.

1.2. Types of conducting polymers

Conducting polymers can be classified mainly into three types:

a) Intrinsically / inherently conducting polymers.

b) Conducting polymer composites.

c) Ionically conducting polymers.

An organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processibility

etc. commonly associated with a conventional polymer, is termed an “Intrinsically Conducting Polymer” more commonly known as “synthetic metal” [19].

The most common examples of intrinsically / inherently conducting polymers are Polyacetylene, Polyaniline, Polypyrrole, Polythiophene, Poly(*p*-phenylene), Poly(phenylene vinylene) etc. The Figure 1.1 shows some of the conjugated polymers, which have been studied as intrinsically conducting polymers.

The unique electronic properties of the conjugated polymers are derived from the presence of π - electrons, the wave functions of which are delocalized over a long portion of the polymer chain when the molecular structure of the backbone is planar. It is therefore necessary that there are no large torsion angles at the bonds, which would decrease the delocalization of the π – electrons system [20].

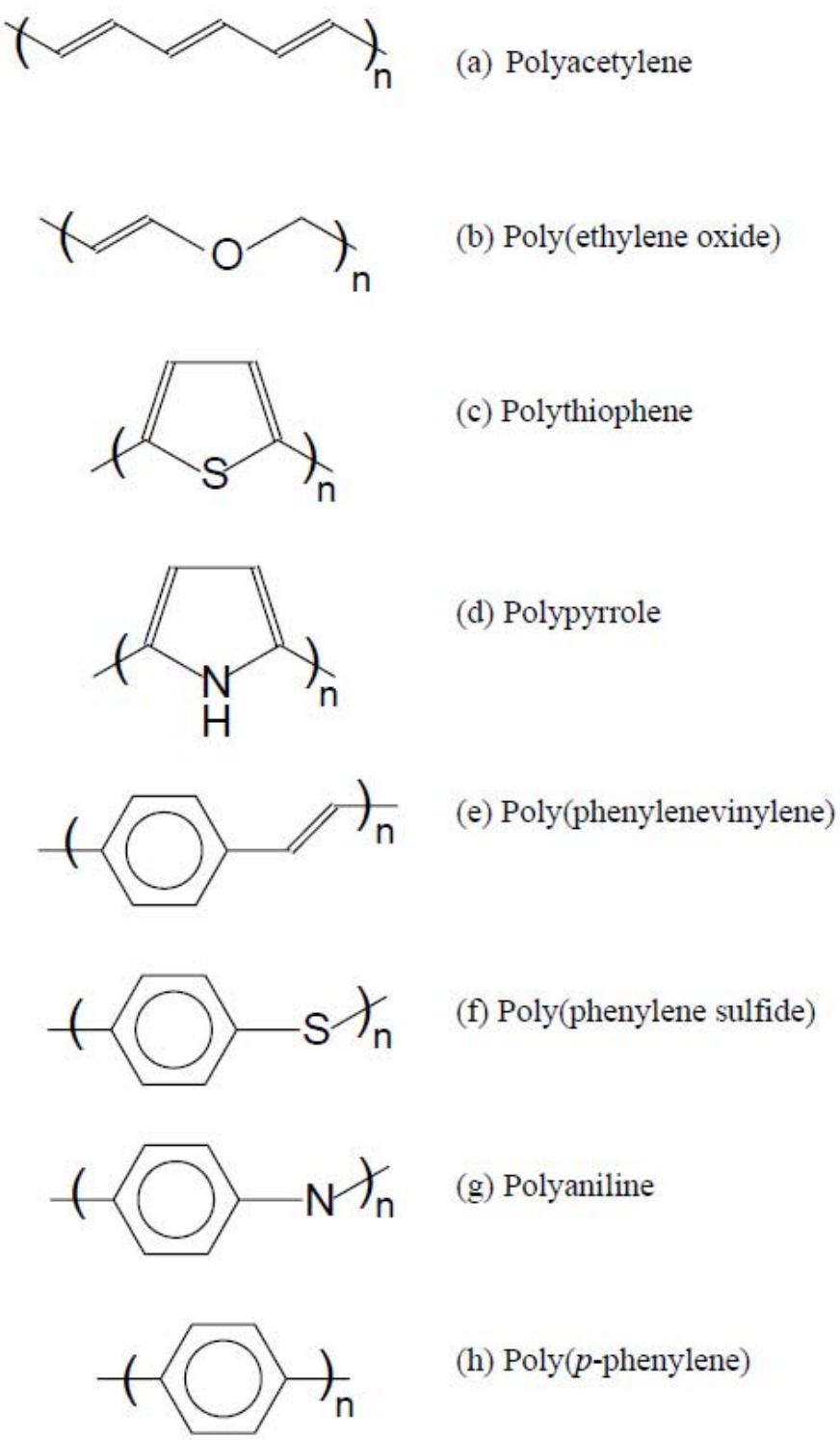


Figure 1.1: Examples of inherently conducting polymers.

1.3. Application of conducting polymers

Researches show that conducting polymers exhibit conductivity from the semiconducting range (~10^{-5} S cm^{-1}) right up to metallic conductivity (~10^{4} S cm^{-1}). With this range of electrical conductivity and low density coupled with low cost polymeric conductor pose a serious challenge to the established inorganic semiconductor technology. There are mainly two groups of applications for organic conducting polymers which are briefly described below:

Group I: These applications just use the conductivity of the polymers. The polymers are used because of either their lightweight, biological compatibility for ease of manufacturing or cost. Electrostatic materials, Conducting adhesives, Electromagnetic shielding, Printed circuit boards, Artificial nerves, Antistatic clothing, Piezoceramics, Active electronics (diodes, transistors), Aircraft structures.

Group II: This group utilizes the electroactivity character property of the materials. Molecular electronics, Electrical displays, Chemical, Biochemical and Thermal sensors, Rechargeable batteries and Solid electrolytes, Drug release systems, Optical computers, Ion exchange membranes, Electromechanical actuators, 'Smart' structures, Switches.

1.4. Syntheses of selected conducting polymers

Various methods [21] are available for the synthesis of conducting polymers. However, the most widely used technique is the oxidative coupling involving the oxidation of monomers to form a cation radical followed by coupling to form di-cations and the repetition leads to the polymer. Electrochemical synthesis is rapidly becoming the preferred general method for preparing electrically conducting polymers because of its simplicity and reproducibility. The advantage of electrochemical polymerization is that the reactions can be carried out at room

temperature. By varying either the potential or current with time the thickness of the film can be controlled.

Electrochemical polymerization of conducting polymers is generally employed by: (1) constant current or galvanostatic; (2) constant potential or potentiostatic; (3) potential scanning/cycling or sweeping methods. Standard electrochemical technique which employs a divided cell containing a working electrode, a counter electrode and a reference electrode generally produces the best films. The commonly used anodes are chromium, gold, nickel, palladium, titanium, platinum and indium-tin oxide coated glass plates. Semi-conducting materials such as n-doped silicon [22], gallium arsenide [23], cadmium sulphide and semi-metal graphite [24] are also used for the growth of polymer films. Electrochemical synthesis can be used to prepare free standing, homogeneous and self doped films. Besides this, it is possible to obtain copolymers and graft copolymers. Polyazulene, polythiophene, polyaniline, polycarbazole and several other polymers have been synthesized using this approach.

1.4.1. Polyaniline

The largest use of aniline and its derivatives is in dye production. They are thus important ingredients in color industry. Every year, thousands of new colors and shades are generated and tested in industry. Polyaniline is one of the oldest artificial conducting polymers [25] and its high electrical conductivity among organic compounds has attracted continuing attention [26]. Aromatic amines are also involved in the search for potentially interesting new compounds in materials science [27].

The anodic oxidation of aniline to the final product, polyaniline, is quite complex and there is still a controversy as regards the reaction pathway. The main question to

be answered concerns the chemical nature of the intermediates. For instance, it was widely believed even in early papers [28] that, in acidic media, the polymerization process involves a coupling of aniline radical cation that is formed in the initial oxidation step. The cation, being an acid, would be stabilized in acidic conditions. Initial intermediate species produced during aniline oxidation (Figure 1.2) have been known to be head-to head, tail-to-tail and head-to-tail type linkages whose molar ratio depends on pH of the medium. Aniline couples mainly tail-to-tail, and head-to-tail under acidic conditions. However the head-to-head coupling reported at high pH values.

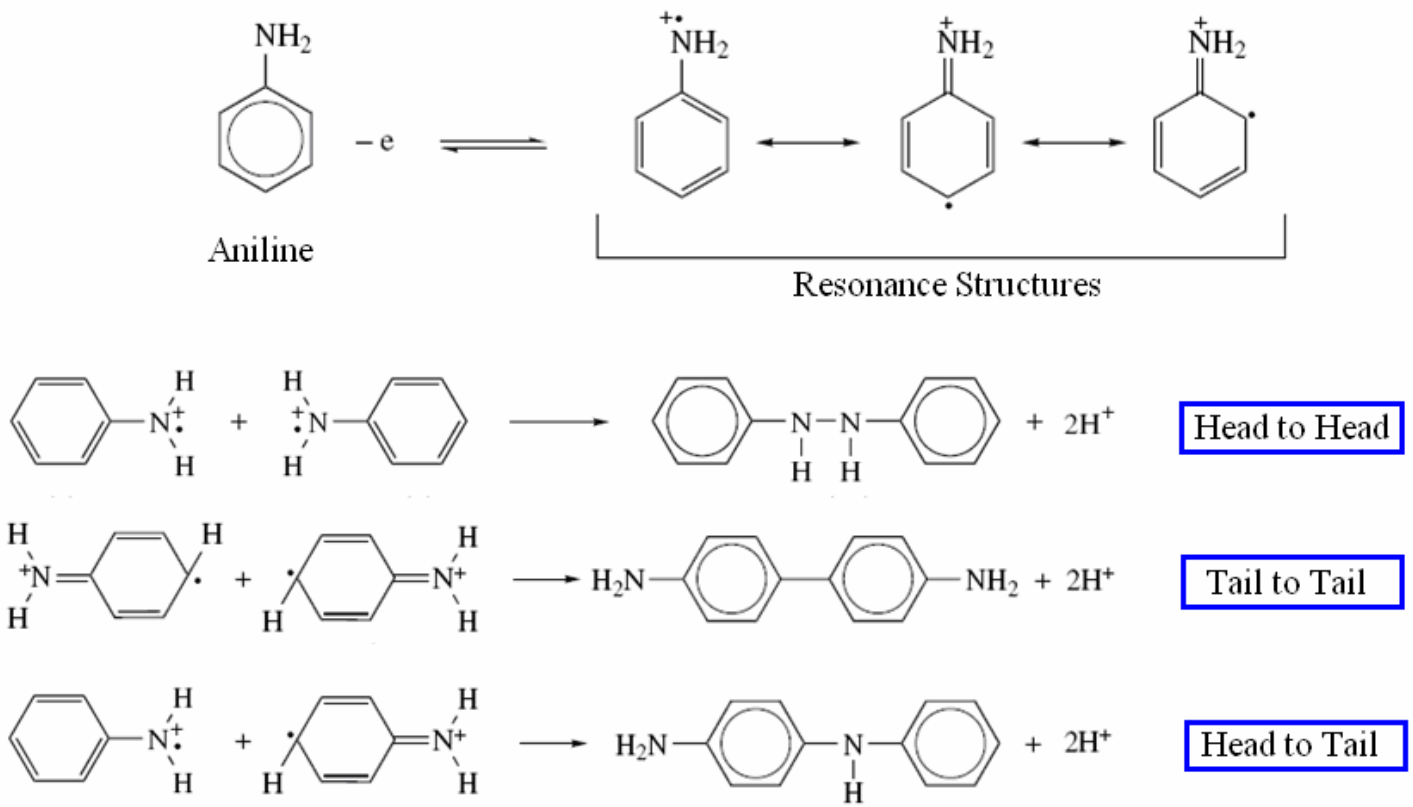


Figure 1.2: Resonance structure of aniline and initial intermediate species produced during aniline oxidation.

Polyaniline is composed of aniline repeat units connected to form a backbone. The existence of a nitrogen atom lying between phenyl rings allows the formation of different oxidation states (doping) that can affect its physical properties. In general, three distinct forms are available, depending on the degree of oxidation of the nitrogens (Figure 1.3):

(a) A leucoemeraldine base is a fully reduced form which contains only benzene rings in the polymer chain.

(b) An emeraldine base is a half oxidized form, where both benzene and quinoidal rings are present.

(c) A pernigraniline base is a fully oxidized form.

The conducting emeraldine salt form can be obtained by oxidative doping of leucoemeraldine base or by protonation of emeraldine base (Figure 1.4).

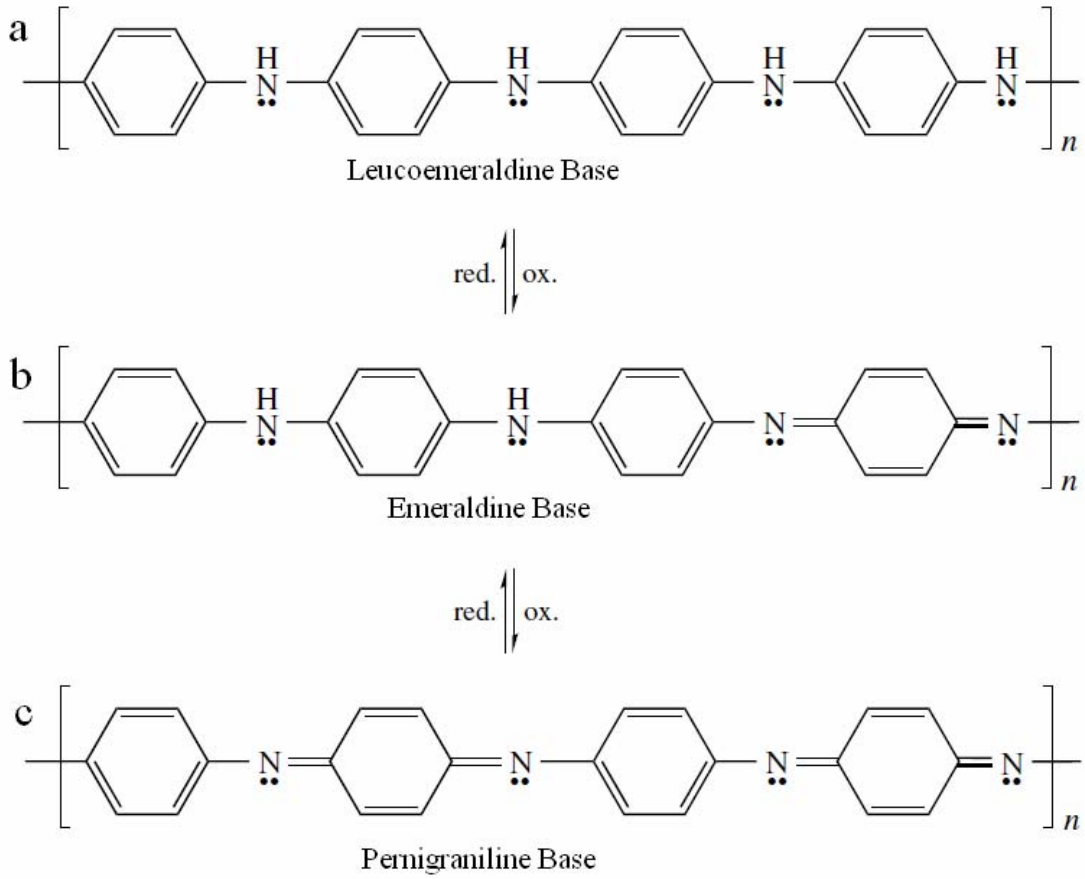


Figure 1.3: Different forms of polyaniline.

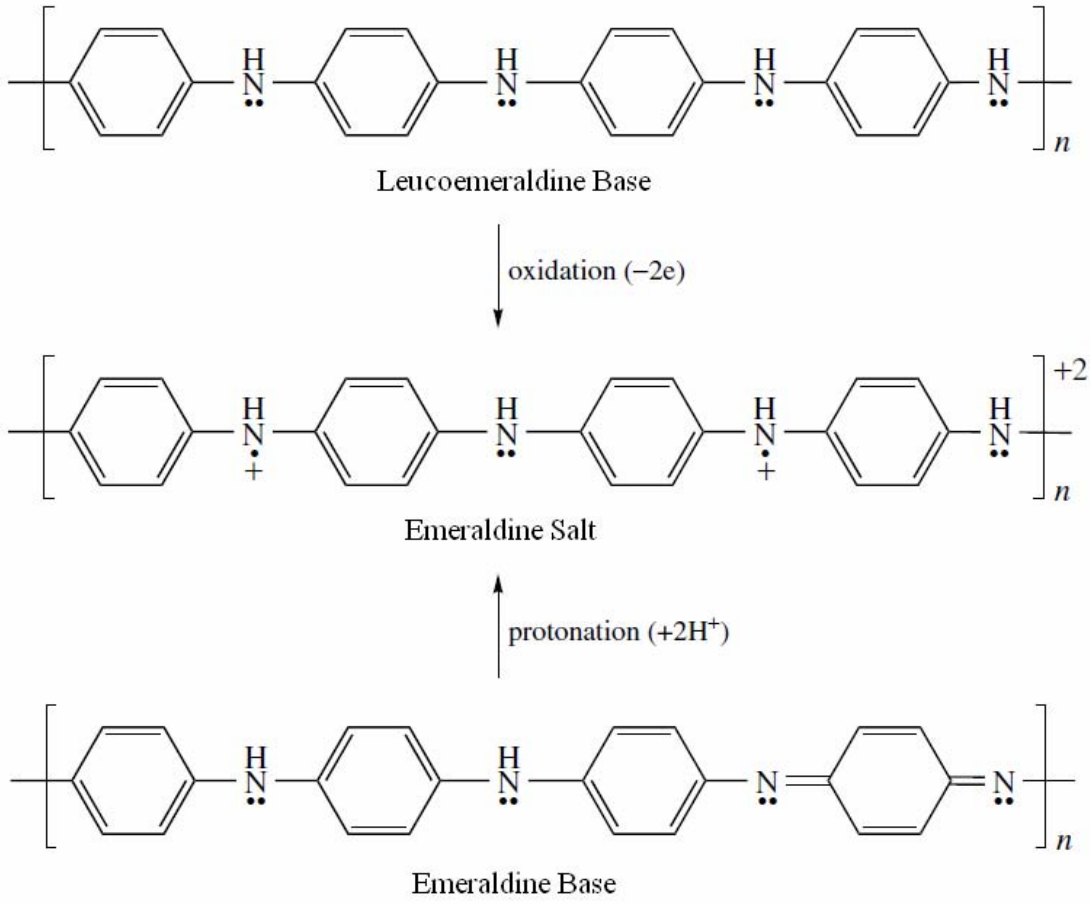


Figure 1.4: Formation of a polyaniline salt following oxidation and protonation of bases.

Electrically conducting polymers in their pristine and doped states have been the materials of great interest for their applications in modern technologies. Among all conducting polymers polyaniline has a special representation, probably due to the fact that new applications of polyaniline in several fields of technology are expected. Although polyaniline is one of the most important conducting polymers around, detailed study on its structure and properties only begun in the 1980s [29-35].

Generally, it is accepted that polyaniline is a redox polymer. Figure 1.5a shows this blend where polyaniline has both the reduced benzenoid unit (y) and the oxidized quinoid unit (1 – y) [36]. Polyaniline may exist in several oxidation states, i.e. from the completely reduced leucoemeraldine state (Figure 1.5b), where 1 – y = 0, to the completely oxidized pernigraniline state, where 1 – y = 1. The half-oxidized emeraldine base state, where 1 – y = 0.5, is composed of an alternating sequence of two benzenoid units and one quinoid unit [37, 38]. Even though each of these three states of polyaniline possesses quite interesting physical and chemical properties, they, actually, are insulators. However, the insulator blue emeraldine base may be conducting if it is doped with protic acids and become green protonated emeraldine or emeraldine salt with dc conductivity in the metallic region (ca. 1~5 S cm^{-1}) [39]. The later may also be obtained via a redox doping process of either its corresponding reduced leucoemeraldine or oxidized pernigraniline, by either a chemical or an electrochemical step in acid conditions (Figure 1.5b). The deprotonation of emeraldine salt revert this to emeraldine base.

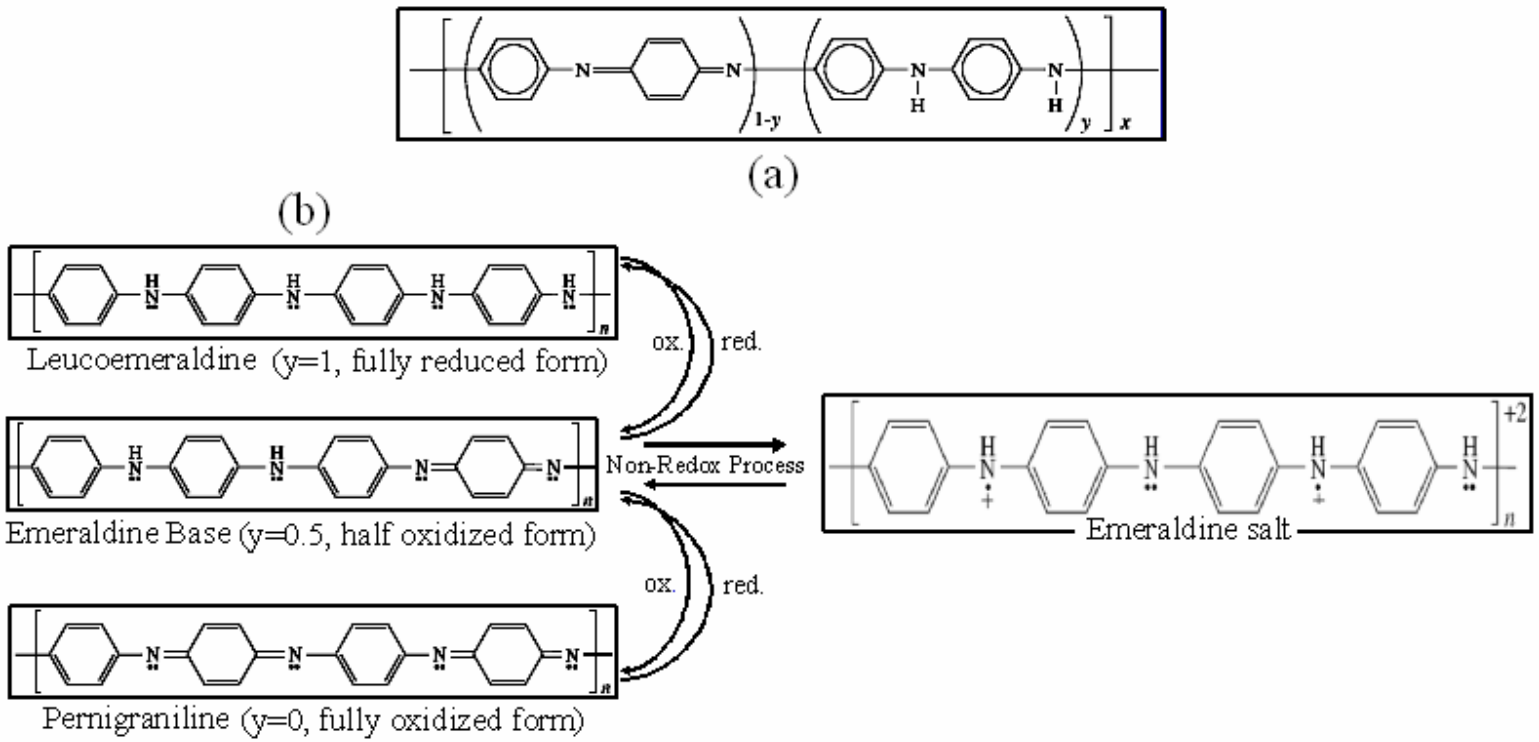


Figure 1.5: Various states of oxidation and protonation of polyaniline.

Polyaniline is prepared either by chemical or electrochemical oxidation of aniline under acidic conditions. The method of synthesis depends on the intended application of the polymer. Whenever thin films and better patterns are required, an electrochemical method is preferred.

1.4.1(a) Chemical synthesis

Chemical polymerization of aniline has been carried out in an acidic solution [40-44]. This acidic condition provides the solubilization of the monomers as well as the formation of emeraldine salt as a conducting polyaniline. Figure 1.6 depicts a chemical polymerization mechanism of aniline in acidic solution using an oxidizing agent. Aniline monomer forms the anilinium ion in acidic medium and chemical polymerization results in the formation of protonated, partially oxidized form of polyaniline. The initial step involves formation of the aniline radical cation. The next step is followed by the coupling of N- and para-radical cations with consecutive rearomatization of the dication of *para*-aminodiphenylamine. The oxidation process of the diradical dication makes the fully oxidized pernigraniline salt form of polyaniline due to the high oxidizing power of the oxidant such as ammonium persulfate ($(NH_4)_2S_2O_8$). Whereas “head-to-tail” coupling is predominant, some coupling in the *ortho*-position also occurs, leading to conjugation defects in the final product.

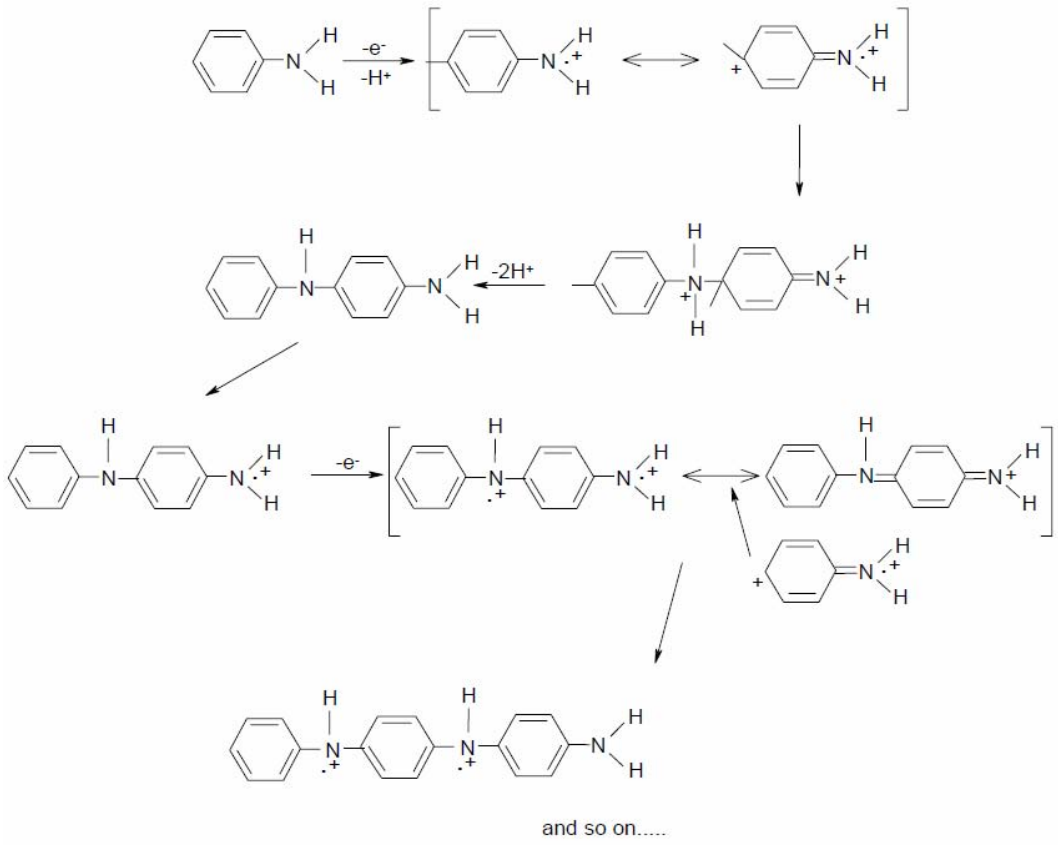


Figure 1.6: Polymerization mechanism of aniline [45].

After consuming all the oxidant, the unreacted aniline monomer reduces the pernigraniline to produce the green emeraldine salt as the resultant polymer. From the viewpoint of color change in solution, the formation of *para*-aminodiphenylamine reflects pink, and the formation of protonated pernigraniline becomes deep green. Green emeraldine salt precipitates after reduction of pernigraniline in the final step. In the termination step, green emeraldine salt forms as a conductive polyaniline form and it can be converted to emeraldine base with an alkaline solution or an excess of water. The emeraldine base can be transformed to two non-conductive polyaniline such as the completely oxidized pernigraniline and reduced leucoemeraldine depending on oxidation states. Imine sites of the emeraldine base are easily protonated in acid condition, which results in the formation of green emeraldine salt as a conducting polyaniline [46]. The conductivity of polyaniline was affected by degree of protonation and oxidation. In addition, the structural and conformational factors derived from polymerization condition also affect the conductivity of polyaniline.

1.4.1(b) Electrochemical synthesis

Electrochemical synthesis of polyaniline is a radical combination reaction and is diffusion controlled. Electropolymerization is generally carried out in aqueous protonic acid medium and this can be achieved by any one of the methods given here:

i) Galvanostatic: constant current in the range of 1-10 mA.

ii) Potentiostatic: at constant potentials −0.7 to 1.1 V versus SCE.

iii) Sweeping the potential: between two potential limits −0.2V to +1.0V vs. SCE.

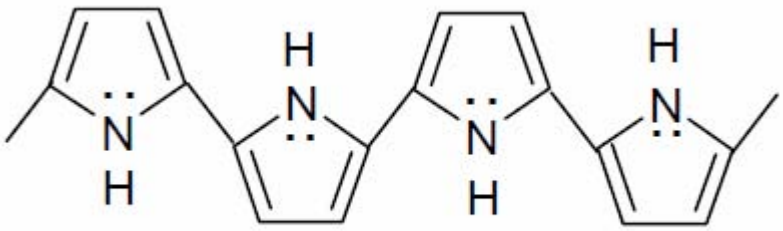
In the case of Ani electropolymerization, the radical cation of aniline monomer is formed on the electrode surface by oxidation of the monomer [40, 47-50]. This process is considered to be the rate-determining step. Radical coupling and

elimination of two protons make mainly paraformed dimers. Chain propagation proceeds with oxidation of the dimer and aniline monomer on the electrode surface. In this step, the radical cation of the oligomer couples with a radical cation of aniline monomer. In the final step, polyaniline is doped by the acid present in solution. The growth of polyaniline has been considered to be self catalyzed. This means that the polymers are formed at the higher rate as the more monomers are deposited onto the polymer surface. It involves the adsorption of the anilinium ion onto the oxidized form of polyaniline, followed by electron transfer to form the radical cation and subsequent reoxidation of the polymer to its most oxidized state.

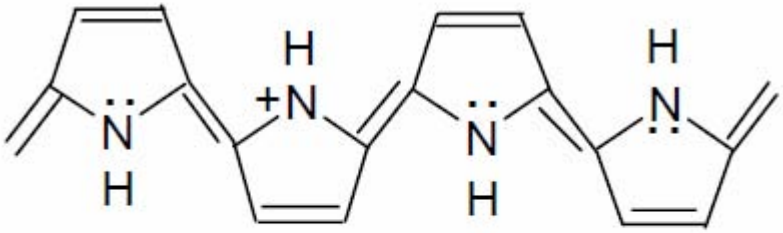
1.4.2. Polypyrrole

Polypyrrole is an inherently conductive polymer due to excluded π conjugation of electrons, which is stabilized by the heterocyclic group. Polypyrrole is an especially promising conductive polymer for commercial applications, owing to its high conductivity, good environmental stability and ease of synthesis. It is easy to prepare by standard electrochemical techniques and its surface charge characteristics can easily be modified by changing the dopant anion that is incorporated into the material during synthesis.

Conducting polypyrrole can be prepared by various methods such as chemical, electrochemical, vapor phase etc. The different two oxidation states of polypyrrole are shown in the Figure 1.7.



Aromatic Structure



Quinoid Structure

Figure 1.7: Various oxidation states of polypyrrole.

1.4.2(a) Chemical synthesise

Polypyrrole has been prepared in the presence of various oxidizing agents like sulfuric acid, nitrous acid, quinones or ozone. The material obtained was in the insulating range 10^{-10} to 10^{-11} S cm^{-1} [51]. This could be then doped with halogenic electron acceptors such as bromine and iodine to achieve a stable conductivity of 10^{-5} S cm^{-1} [52].

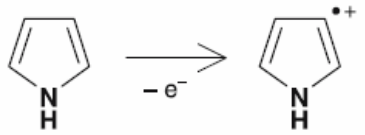
In recent times, polypyrrole is synthesized chemically in conducting state, because the polymer oxidation occurs with oxidant salts acting as dopant agents. Several metallic salts such as $FeCl_3$, $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$, $CuCl_2$ and $CuBr_2$, have been employed for the polymerization of pyrrole [53-55]. Ferric salts are the most commonly used oxidants for the chemical synthesis of highly conductive polymer complexes.

Figure 1.8 describes a typical mechanism for chemical oxidation polymerization of pyrrole. In the initiation step, radical cations ($C_4NH_5^+$) are generated by the oxidation of pyrrole monomer. A radical-radical coupling occurs between two radical cations, and forms a dimer with deprotonation, leading to a bipyrrole. The bipyrrole is reoxidized and couples with other radical cations. This process is repeated consecutively during the propagation step. The termination takes place due to the nucleophilic attack of water molecules or impurities in the polymer chains.

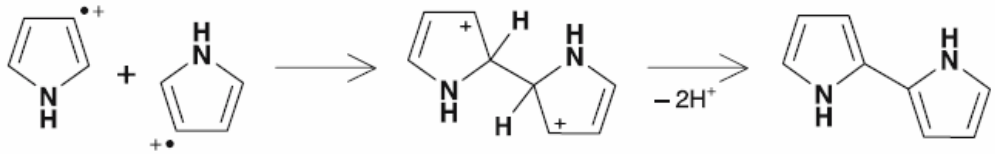
1.4.2(b) Electrochemical synthesis

It is reported that [56] the electrosynthesis of polypyrrole film proceeds via the oxidation of pyrrole at the platinum electrode to produce an unstable P-radical cation which then reacts with the neighboring pyrrole species. The cyclic voltammograms of these solutions show an irreversible peak for the oxidation of pyrrole at +1.2 V versus the saturated calomel reference electrode (SCE) [57].

1. *Oxidation of monomer*



2. *Radical coupling*



3. *Chain propagation*

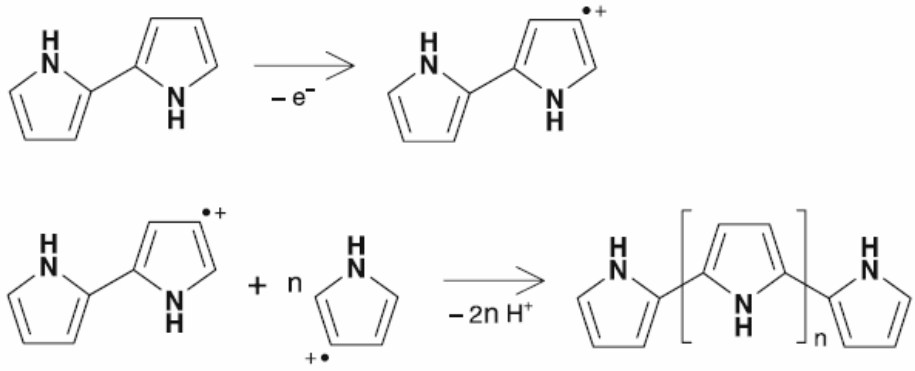


Figure 1.8: Polymerization mechanism of pyrrole [58].

The mechanism of the overall reaction for the formation of fully aromatized product is very complicated and involves series of oxidation and deprotonation steps. In practice polypyrrole films are prepared by the electro-oxidation of pyrrole in one compartment cell equipped with platinum working electrode, gold wire counter electrode and a saturated calomel reference electrode. A wide variety of solvents and electrolytes can be used as the electrical resistance of the solution is high and the nucleophilicity does not interfere with the polymerization reaction. These conditions can be accomplished by selecting solutions where the electrolyte is highly dissociated and which are slightly acidic. Films of various thicknesses can be prepared by changing the current density. Many other authors have investigated the process of electrochemical deposition of conducting polypyrrole [59].

1.4.2(c) Vapour phase deposition

This technique, although known for depositing polypyrrole films since about a decade ago [60]. The gas phase preparation of polypyrrole has been described by Chen et al. [61]. Conducting polymer films were prepared in a similar manner to the chemical vapor deposition method [60]. The polypyrrole films were prepared in two ways i.e. by vapor phase polymerization using H_2O_2 or HCl, or by chemical vapor deposition of polypyrrole doped with $FeCl_3$. Bhattacharya and Misra [62] have used polyvinyl chloride-cupric chloride complex film as base polymer and polypyrrole was vapor phase polymerized on this. Wang et al. [63] have also made polypyrrole films by this method. They used polyethyleneoxide and $FeCl_3$, which were first dissolved in a suitable solvent, from which, films were cast on glass slides. These were dried and exposed then exposed to pyrrole vapors. The sample showed in-situ growth of polypyrrole films, which also developed crystalline order.

1.4.3. Poly-*ortho*-phenylenediamine

The polymers of aromatic diamines including phenylenediamines, diaminonaphthalenes, diaminoanthraquinones, benzidine, naphthidine, and diaminopyridine have received increasing attention. These monomers are very susceptible to oxidative polymerization via oxidation of one or both amino groups to give linear polyaminoaniline, linear polyaminonaphthylamine, ladder polyphenazine, and phenazine unit containing polymers. It is believed that investigations on the aromatic diamine polymers are more attractive since they exhibit more novel multifunctionality than polyaniline and polypyrrole. The polymers have shown apparently different characteristics versus widely researched conducting polymers such as polyaniline and polypyrrole in the application of electrocatalysis, electrochromics, sensors, electrode materials, heavy metal ion complex, and detection [64-66], although the polymerization mechanism and properties of the polymers have not been definitely reported. It should be appreciated that the aromatic diamine polymers possess good multifunctionality partially due to one free amino group per repetitive unit on the polymers. Most of the polymers of the aromatic diamines have been prepared by electrochemical polymerization, but only a small number of polymers were obtained through chemically oxidative polymerization.

1.4.3(a) Chemical synthesis

Thus far, only a few reports have described the formation of polymeric products by chemical oxidation of aromatic diamines. However, relatively few reports have appeared on the synthesis and structure of the polymers from aromatic diamines prepared by chemically oxidative polymerization. The oxidative polymerization was generally accomplished as follows: first, phenylenediamine monomers and oxidant were separately dissolved in acidic aqueous solutions. Then

the polymerization reaction was initiated by steadily adding oxidant solution drop wise into the monomer solution at 25-30 °C for *meta*-phenylenediamine and *para*-phenylenediamine in common inorganic or organic acidic aqueous solutions and 118 °C for *ortho*-phenylenediamine only in glacial acetic acid. The drop wise addition of oxidant solution is beneficial for obtaining polymers with a relatively high molecular weight and narrow molecular weight distribution because the oxidation polymerization of the aromatic diamines is highly exothermic. Finally, the reaction continued for at least 12 h. The resulting powder product was filtered and dried at temperatures lower than 60 °C. A drying temperature of higher than 60 °C might lead to cross-linking of the polymers. The acids used for the preparation of aromatic diamine polymers mainly include HCl and glacial acetic acid. The effective oxidants are persulfate, iodine, H_2O_2, ceric ammonium nitrate, and $Cu(NO_3)_2$. Among them, the persulfates including Na^+, K^+, and NH_4^+ persulfates are commonly employed as oxidizing agents. Note that the oxidant is not necessary to the chemical oxidative polymerization of *meta*-phenylenediamine and *para*-phenylenediamine. For example, *meta*-phenylenediamine and *para*-phenylenediamine in oxidant-free acetic acid aqueous solution can polymerize into polymers with the characteristics of semiconductors at polymerization yields of 15% and 60%, respectively. However, the oxidant is required for the chemically oxidative polymerization of *ortho*-phenylenediamine because no oxidative polymer of *ortho*-phenylenediamine can be obtained even if reaction at flux temperature in acetic acid aqueous solution is allowed to proceed for 8 h. Moreover, the oxidative polymerization yield of *ortho*-phenylenediamine is usually the lowest and the yield of *para*-phenylenediamine the highest [67].

1.4.3(b) Electrochemical synthesis

Polarographic investigations of *ortho*-phenylenediamine were reported with gold, graphite, and platinum electrodes in HCl and buffer (pH=1–4) solutions, and the oxidation potential, critical oxidation potential, and polarographic half-wave potential of *ortho*-phenylenediamine were given first by Lord and Rogers in 1954 [68]. Parker and Adams examined the anodic polarography of three phenylenediamines (*ortho*, *meta* and *para*) on a rotating Pt electrode using a current-scanning technique in 1956 [69]. They observed a linear relationship between limiting current and *para*-phenylenediamine concentration. The electropolymerization mechanism of three phenylenediamines was first suggested by Elving and Krivis in 1958 [70]. They proposed that the oxidation mechanism of three phenylenediamines depends on the phenylenediamine monomer structure and solution pH value [71].

Poly-*ortho*-phenylenediamine can be prepared electrochemically in acid, neutral and alkaline solutions and is very stable in both aqueous solutions and air [72, 73]. The ease of dissolution of poly-*ortho*-phenylenediamine in organic solvents such as dimethyl sulfoxide makes it one of the so-called soluble electroactive polymers and thus provides more flexibility in the studies of its structures [73-76]. Electrochemical techniques, insitu FTIR spectroscopy [73, 77], resonant Raman spectroscopy [78], radiometry [79], the electrochemical quartz crystal microbalance (EQCM) [80] and other methods have been employed to study the electropolymerization mechanism, to characterize the polymer films and to develop various applications of poly-*ortho*-phenylenediamine.

During the electropolymerization process, polymer film is deposited on the electrode surface and the formation of soluble oligomers might occur. The local concentration of the oligomers near the electrode surface might be very high,

depending on the solubility and the diffusivity of the oligomers. The polymer films formed might be very porous.

Generally, *ortho*-, *meta*-, and *para*-phenylenediamines undergo oxidative polymerization to give phenazine ring containing ladder polymers with free amino groups [72, 75, 76]. Rothwell and co-workers [72] proposed a ladder-like, asymmetrical "quinoid" structure with phenazine-like units, while Yano and Yamasaki [74] suggested a ring-opened 1,4-substituted benzenoid-quinoid structure. The mechanisms of electropolymerization were very complicated in nature [72, 74]. poly-*ortho*-phenylenediamine film should possess a mixture of ladder-like and ring-opened structures (Figure 1.9).